

AD-A104 398

VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY
A REINVESTIGATION OF THE REACTIONS OF ENOLATE ANIONS WITH CYCLO--ETC(U)
SEP 81 C W ALLEN, K RAMACHANDRAN, R P BRIGHT N00014-77-C-0605

F/B 7/3

ML

UNCLASSIFIED TR-9

A
00014-77-C
TR-9

END
DATE FILMED
40-81
OTIC

DTIC FILE COPY

AD A104398

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO. AD-A104	3. RECIPIENT'S CATALOG NUMBER 398
4. TITLE (and Subtitle) A Reinvestigation of the Reactions of Enolate Anions with Cyclotriphosphazenes		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Christopher W. Allen, Kolikkara Ramachandran Randall P. Bright and Jonathan C. Shaw		8. CONTRACT OR GRANT NUMBER(s) N001477C-0605
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Vermont Burlington, Vermont 05405		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research, Arlington, VA 22217		12. REPORT DATE 9/9/81
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		14. NUMBER OF PAGES 5
		15. SECURITY CLASS. (of this report) Unclassified
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release and sale; its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) A JUL 13 1981		
18. SUPPLEMENTARY NOTES Submitted for publication in Inorganic and Nuclear Chemistry Letters		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) phosphazenes enolate anions nmr organofunctional phosphazenes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reactions of enolate anions with hexachlorocyclotriphosphazenes have been reexamined. Based on N.M.R. spectroscopic data, structures of the type $N_3^+P(X^+)_3^+OCR=CH_2^-$ ($X=F, Cl; R=H, C_6H_5$) are proposed.		

OFFICE OF NAVAL RESEARCH

Contract N001477C-0605

Project NR 356-663

9) Technical Report No. 9

14) TR-9

(6)

A Reinvestigation of the Reactions of Enolate Anions
with Cyclotriphosphazenes,

By

(10)

Christopher W. Allen, Kolikkara Ramachandran,
Randall P. Bright ~~and~~ Jonathan C. Shaw

Prepared for Publication in
Inorganic and Nuclear Chemistry Letters

(12) 22

University of Vermont
Department of Chemistry
Burlington, Vermont 05405

(13)

NOM14-77-2-0605

A

Reproduction in whole or in part is permitted for any purposes of the
United States Government.

This document has been approved for public release and sale; its distribution
is unlimited.

A REINVESTIGATION OF THE REACTIONS
OF ENOLATE ANIONS WITH CYCLOTRIPHOSPHAZENES

Christopher W. Allen, Kolikkara Ramachandran,
Randall P. Bright and Jonathan C. Shaw
Department of Chemistry
University of Vermont,
Burlington, Vermont 05405

Abstract

The reactions of enolate anions with hexahalocyclotriphosphazenes have been reexamined. Based on N.M.R. spectroscopic data, structures of the type $N_3P_3X_5OCR=CH_2$ ($X=F, Cl$; $R=H, C_6H_5$) are proposed.

Introduction

Enolate anions of ketones are ambident nucleophiles which have attracted considerable attention (1). We have previously reported the reactions of the lithium enolate anions of acetophenone and cyclohexanone with hexafluorocyclotriphosphazene, $N_3P_3F_6$, and based on limited nmr data suggested that attack occurred at the carbon end of the nucleophile leading to ketones with the phosphazene moiety bonded to the α -carbon atom (2). Recently, Tate et.al. reported the reactions of polydichlorophosphazene with various enolate anions and proposed that attack occurred at the oxygen end of the nucleophile (3), thus leading to vinyl alcohol derivatives. This investigation is an attempt to resolve these conflicting interpretation concerning the nature of these materials.

Experimental

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (Ethyl Corp.) was recrystallized from petroleum ether to a constant m.p. 113°C n-Butyl lithium (1.6M solution in hexane) was obtained from Aldrich. Tetrahydrofuran (THF) (Aldrich) was distilled from sodium-benzophenone ketyl. Petroleum ether (b.p. 35-55°C), benzene and ethyl acetate (Fisher) were distilled by standard procedures. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 MHz (1H), 62.9 MHz (^{13}C), and 101.2 MHz (^{31}P). Tetramethyl silane (TMS) was used as an internal reference for 1H and ^{13}C NMR measurements. For ^{31}P NMR, 85% H_3PO_4 was used as an external standard. Chemical shifts upfield to the reference are assigned a negative sign. ^{13}C and ^{31}P NMR spectra were recorded under conditions of broad band decoupling. Infrared (IR) spectra were obtained as their thin films (NaCl discs) on a Beckman IR 20A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories. Hexafluorocyclotriphosphazene (4) and the derivatives derived from

the enolate anions of acetophenone (I, $N_3P_3F_5OC_8H_7$) and cyclohexanone (II, $N_3P_3F_5OC_6H_9O$) (2) were prepared by previously reported procedures.

Preparation of $N_3P_3Cl_5OCH=CH_2$ (III). A solution of n-butyl lithium (45 mL, 0.07 mol) was added to tetrahydrofuran (THF) (75 mL) at room temperature, using the apparatus described elsewhere (5). The resulting reaction mixture was stirred for 16 hr then slowly added to a solution of 10.5 g (.03 mol) of $N_3P_3Cl_6$ in tetrahydrofuran at 0°C under a nitrogen atmosphere. The resulting mixture was allowed to come to room temperature and was kept stirred for four days. The solvent was removed and the residue extracted with hexane. Following filtration and removal of hexane, 10.2 g of a pale yellow liquid was obtained. A 2 gm sample of this material was purified using the flash chromatography technique (6) using petroleum ether as the eluant. A 0.92 g (44.3% of theory) sample of a colorless liquid, b.p. 75° at 0.05 mm Hg was obtained. Anal. Calcd. for $N_3P_3Cl_5OC_2H_3$ (III): C, 6.75; H, 0.84; mol wt 353. Found: C, 6.74; H, 0.75; mol wt 353 (mass spectrum).

IR(cm^{-1}): 1650(s, C=C str), 1220(s, PN str), 1110(s, PO str), 1035(s), 930(w, PCl), 875(m, PCl) 750(m, PCl).

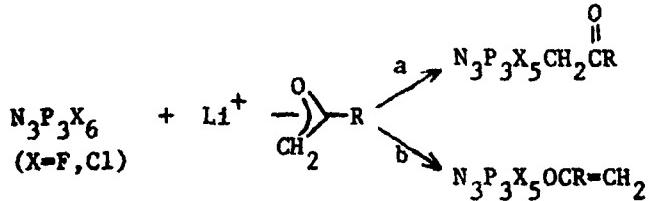
Preparation of $N_3P_3F_5OCH=CH_2$ (IV). The reaction of 40 mL (0.064) of n-butyl lithium solution in excess THF was added to 16.0 g (0.064 mol) of $N_3P_3F_6$ as previously described. After removal of most of the solvent, the remaining product/solvent mixture was carefully fractionated at room temperature. The remaining solvent distilling at 5 mm Hg and the product at 1 mm Hg. A sample of 0.56 g (3.2% of theory) of a colorless liquid was obtained. Anal. Calcd. for $N_3P_3F_5OC_2H_3$ (IV): mol wt 273. Found: mol wt 273 (mass spectrum).

IR(cm^{-1}): 1645(m, C=C), 1290(s, PN str), 1125(s, PO str), 1060(m), 1010(m), 950(s, PF asym), 880(s), 845(s, PF), 800(m).

Attempted Derivatization of I and II. In separate experiments, the acetophenone (I) and cyclohexanone (II) derivatives of $N_3P_3F_6$ were treated with bromine (Br_2/CCl_4) and hydrogen ($H_2/10\% Pt$ on activated carbon). In both the bromination and hydrogenation experiments, a large number of products formed which resisted separation.

Results and Discussion

The two possible reaction pathways for the ambident enolate anions with a hexahalocyclotriphosphazene are shown below. Our first attempt at resolving this question involved derivatiza-



tion with bromine on hydrogen. If the vinyloxy (route b) derivative formed, then the simple addition compounds would be readily identifiable. Unfortunately, these reactions gave rise to a large number of products so we turned our attention to nmr spectroscopic techniques. In order to gain more useful information from the nmr studies, we prepared derivatives containing hydrogen

TABLE
Selected N.M.R. Data^a

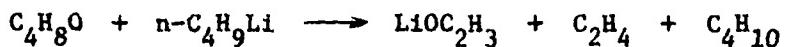
13C

31P

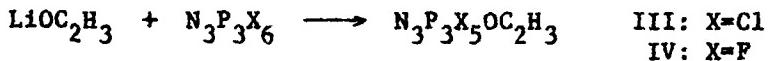
Compound	Selected N.M.R. Data ^a	13C	31P
$\equiv\text{P}(\text{F})\text{OC}_1=\text{C}_2-\text{H}_a-\text{C}_2-\text{H}_b$	(I)	$\delta\text{H}_a = 5.19$; (COMPLEX MULTIPLET) $\delta\text{H}_b = 5.43$; (COMPLEX MULTIPLET)	$\delta\text{C}_1 = 152.43$, $^2\text{J}_{\text{PC}} = 7.94$ $\delta\equiv\text{PF} = 14.84$, $^1\text{J}_{\text{PF}} = 907.43$ $\delta\text{C}_2 = 100.11$, $^3\text{J}_{\text{PC}} = 5.28$ $\delta\equiv\text{PF}_2 = 10.02$, $^1\text{J}_{\text{PF}} = 937.55$
$\equiv\text{P}(\text{F})\text{OC}_1=\text{C}_2-\text{H}_a-\text{C}_2-\text{H}_b$	(II)	$\delta\text{H}_a = 5.58$; (COMPLEX MULTIPLET)	$\delta\text{C}_1 = 147.95$, $^2\text{J}_{\text{PC}} = 9.24$ $\delta\equiv\text{PF} = 15.52$, $^1\text{J}_{\text{PF}} = 919.01$ $\delta\text{C}_2 = 114.49$, $^3\text{J}_{\text{PC}} = 6.40$ $\delta\equiv\text{PF}_2 = 10.30$, $^1\text{J}_{\text{PF}} = 932.13$
$\equiv\text{P}(\text{Cl})\text{OC}_1=\text{C}_2-\text{H}_a$	(III)	$\delta\text{H}_x = 6.55$, $^3\text{J}_{\text{HH}} = 13.43$, $^3\text{J}_{\text{HP}} = 7.63$ $^3\text{J}_{\text{HR}} = 5.80$	$\delta\text{C}_1 = 140.21$, $^2\text{J}_{\text{PC}} = 7.40$ $\delta\equiv\text{PCl}_2 = 13.24$, $^2\text{J}_{\text{PP}} = 64.70$
$\equiv\text{P}(\text{F})\text{OC}_1=\text{C}_2-\text{H}_a$	(IV)	$\delta\text{H}_a = 5.16$; $^3\text{J}_{\text{HH}} = 13.43$, $^4\text{J}_{\text{HP}} = 2.75$ $^2\text{J}_{\text{HH}} = 2.44$ $\delta\text{H}_b = 4.89$; $^3\text{J}_{\text{HH}} = 5.80$, $^4\text{J}_{\text{HP}} = 2.59$ $^2\text{J}_{\text{HH}} = 2.44$ $^3\text{J}_{\text{HH}} = 5.80$ $^3\text{J}_{\text{HP}} = 7.02$ $^3\text{J}_{\text{HP}} = 104.27$, $^3\text{J}_{\text{PC}} = 14.80$ $\delta\equiv\text{PF} = 23.36$, $^2\text{J}_{\text{PP}} = 63.48$ $\delta\text{C}_1 = 140.29$, $^2\text{J}_{\text{PC}} = 6.27$ $\delta\equiv\text{PF} = 11.18$, $^1\text{J}_{\text{PP}} = 887.67$	$\delta\text{C}_2 = 104.27$, $^3\text{J}_{\text{PC}} = 14.80$ $\delta\equiv\text{PF} = 23.36$, $^2\text{J}_{\text{PP}} = 63.48$ $\delta\text{C}_1 = 140.29$, $^2\text{J}_{\text{PC}} = 6.27$ $\delta\equiv\text{PF} = 11.18$, $^1\text{J}_{\text{PP}} = 887.67$

- a. All coupling constants are given in Hz
- b. ^1H and ^{13}C chemical shifts are given in ppm relative to TMS
- c. chemical shifts are given in ppm relative to 85% H_3PO_4

atoms on both carbon atoms. The enolate anion of acetaldehyde is quantitatively generated from the metalation of THF with n-butyl lithium (7).



and gives derivatives of both the hexachloro- and hexafluorocyclotriphosphazene. The nmr data



(^1H , ^{13}C , ^{31}P) for compounds I-IV are reported in the table.

The ^1H nmr spectrum of III closely resembles that of vinyl acetate except for the additional phosphorus coupling for each proton and can be analyzed as such. The observed spectrum is not consistent with a carbon bonded derivative since H_x exhibits more extensive coupling than it would as an aldehyde proton. The chemical shifts are more appropriate for olefinic rather than for alkyl and aldehyde protons. The same arguments apply to IV. The previous ^1H nmr data on compounds I and II were obtained at 60 MHz and were poorly resolved (2). In the 250 MHz spectrum, the additional coupling appropriate to an olefin but not to an α -substituted ketone, is observed. The separation between H_a and H_b in I is too large to be ascribed to J_{PCH} in an alkylphosphazene (8). Furthermore, only H_a is observed in II, thus the two peaks (H_a , H_b) observed in I are not reasonably ascribed to phosphorus-proton coupling. The strongest evidence favoring the bonding of the enol form comes from the ^{13}C nmr data. There are no resonances in the alkyl or carbonyl ranges (9) while those in the olefin range match the number predicted from a vinyloxy derivative. The assignments of C_1 and C_2 shifts in III were confirmed by off resonance decoupling in which C_1 becomes a doublet and C_2 a triplet. The large shielding of C_1 is due to mesomeric interactions of C_1 with oxygen lone pair electrons (9). The magnitude of the phosphorus-carbon coupling constants is variable and doesn't provide a useful structural tool in this case. The ^{31}P nmr spectra of I-IV show little variation with or without broad band proton decoupling. If the phosphorus atom were bonded to a methylene group, significant J_{PCH} effects would be observed in the πPXR resonance.

All of the nmr data which we have presented support the proposal of Tate (3) that attack of the enolate is at the oxygen end, rather than at the carbon end, of the nucleophile. The IR data are also consistent with this conclusion. The bands around 1650 cm^{-1} can be ascribed to olefinic stretching modes rather than carbonyl modes and bands around 1130 cm^{-1} can be assigned to a POC vibration rather than unusual PN vibrations. These materials, especially the newly reported III and IV, represent another example of organofunctional phosphazenes (10) which may be expected to exhibit interesting monomer and polymer chemistry. Work along these lines is currently in progress in our laboratory.

Acknowledgements

This work was supported in part by the Office of Naval Research. We also wish to thank Dr. D. P. Tate of Firestone Corp. for useful discussion.

References

1. H. O. HOUSE and V. KROMER, J. Org. Chem. 28, 3362 (1963).
2. J. G. DuPONT and C. W. ALLEN, Inorg. Chem. 16, 2964 (1977).
3. D. P. TATE, W. L. HERGENROTHER, J. W. KANG and D. F. GRAVES, Polymer Preprints 20, 177 (1979).
4. T. MOELLER, K. JOHN and F. Y. TSANG, Chem. Ind. (London) 347 (1961).
5. C. W. ALLEN, R. P. BRIGHT, J. L. DESORCIE, J. A. MACKAY and K. RAMACHANDRAN, J. Chem. Educ. 57, 564 (1980).
6. W. C. STILL, M. KAHN and A. MITRA, J. Org. Chem. 43, 2923 (1978).
7. R. B. BATES, L. M. KROPOSKI and D. E. POTTER, J. Org. Chem. 37, 560 (1972).
8. T. N. RANGANATHAN, S. M. TODD and N. L. PADDOCK, Inorg. Chem. 12, 316 (1973); H. R. ALLCOCK and P. J. HARRIS, J. Am. Chem. Soc. 101, 6221 (1979).
9. J. B. STROTHERS, Carbon-13 NMR Spectroscopy, Academic Press, N. Y. (1972).
10. C. W. ALLEN and J. G. DuPONT, Ind. Eng. Chem. Prod. Res. Dev. 18, 81 (1979).

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U. S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Dr. T. C. Williams Union Carbide Corporation Chemical and Plastics Tarrytown Technical Center Tarrytown, New York	1	Douglas Aircraft Company 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library CI 290/36-84 AUTO-Sutton	1
Dr. R. Soulen Contract Research Department Pennwalt Corporation 900 First Avenue King of Prussia, Pennsylvania 19406	1	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	1
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1	Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. H. Allcock Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1	Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	1	Dr. Martin H. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	1
Dr. R. Lenz University of Massachusetts Department of Chemistry Amherst, Massachusetts 01002	1	Dr. J. Magill University of Pittsburgh Metallurgical and Materials Engineering Pittsburg, Pennsylvania 22230	1
Dr. M. David Curtis University of Michigan Department of Chemistry Ann Arbor, Michigan 48105	1	Dr. D. Bergbreiter Texas A&M University Department of Chemistry College Station, Texas 77843	1
Dr. M. Good Division of Engineering Research Louisiana State University Baton Rouge, Louisiana 70803	1	Professor R. Drago Department of Chemistry University of Illinois Urbana, Illinois 61801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	<u>No.</u>	<u>Copies</u>
Dr. F. Brinkman Chemical Stability & Corrosion Division Department of Commerce National Bureau of Standards Washington, D.C. 20234	1	
Professor H. A. Titus Department of Electrical Engineering Naval Postgraduate School Monterey, California 93940	1	
COL R. W. Bowles, Code 100M Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217	1	
Professor T. Katz Department of Chemistry Columbia University New York, New York 10027	1	
Professor James Chien Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1	
Professor Malcolm B. Polk Department of Chemistry Atlanta University Atlanta, Georgia 30314	1	

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Mr. Keith B. Baucom Director of Contract Research SCM-PCR Incorporated P.O. Box 1466 Gainesville, Florida 32602	1